

Chapter 7

Elementary examples in two electron systems

We now have the machinery to calculate some useful matrix elements in the two electron case.

The following Hamiltonians will be discussed

- i) $H_{el} = C \cdot 1/r_{12}$ (electrostatic interaction)
- ii) $H_{SO} = \sum_i \zeta s_i \cdot l_i$ (spin – orbit interaction)
- iii) $H_{cf} = C \cdot r^t Y_{tp}$ (crystal field interaction)
- iv) $H_m = \mu_B B (L_z + 2S_z)$ (Zeeman effect)

7.1 The electrostatic interaction

The electrostatic interaction between two charged particles is essentially described by the $1/r_{12}$ operator, where r_{12} is the distance between the two particles, see figure 1.6 below.

fig 6.

Using the addition theorem for spherical harmonics we can write the $1/r_{12}$ operator as

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>^{k+1}}} (C_1^{(k)} \cdot C_2^{(k)}) \quad (7.1)$$

$r_{<}$ is the shorter of r_1 and r_2 , and $r_{>}$ is the larger. We note from Eq. (7.1) that the angular part has a familiar form and that the two operators act on different systems (two different electrons), *c.f.* the previous section. The proof of the addition theorem for spherical harmonics can be found in for example Arfken [2] “Mathematical Methods for Physicists” or Edmonds [11] “Angular Momentum in Quantum Mechanics”.

Because the operator Eq. (7.1) does not depend on the spin (quantum number S) and does commute with the total angular momentum L , it is a wise choice to work in the $SLM_S M_L$ -representation. (In atomic physics the names LS-coupling and Russell-Saunders coupling are frequently used).

The matrix elements take the form

$$\begin{aligned} \langle l_1 l_2 L' S' M'_L M'_S | (C_1^{(k)} \cdot C_2^{(k)}) | l_1 l_2 L S M_L M_S \rangle &= \delta_{S'S} \delta_{M'_S M_S} \delta_{L'L} \delta_{M'_L M_L} \times \\ (-1)^{l_1+l_2+L} \left\{ \begin{matrix} l_1 & l_1 & k \\ l_2 & l_2 & L \end{matrix} \right\} \langle l_1 || C_1^{(k)} || l_1 \rangle \langle l_2 || C_2^{(k)} || l_2 \rangle, \end{aligned} \quad (7.2)$$

$$\langle l || C^{(k)} || l \rangle = (-1)^l [l] \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \quad (7.3)$$

where the Eqs. (6.25) and (6.13) have been used. The sum in Eq. (7.1) could appear rather bothersome but because of the $3j$ -symbol in Eq. (7.3) we see that k has the following constraints

$$\left. \begin{array}{l} 0 \leq k \leq 2l \\ k \text{ even} \end{array} \right\} \quad (7.4)$$

We also note see from Eq. (7.1) that the radial and angular parts of the operator has been separated which means that an actual calculation simplifies considerably. The matrix elements are $M_L M_S$ independent, thus we have a spherically symmetric Hamiltonian. Moreover, Eq. (7.2) gives us a matrix which is diagonal, and split the configuration into states characterized by L and S , the so called terms. The term symbol that commonly is used is

$$^{2S+1}L \quad (7.5)$$

The obvious question that immediately arise is how many terms can Eq. (7.2) split for a given configuration, *i.e.* how many terms do we have for a given electron configuration. We have two distinct cases to begin with. i) The system is made up from non-equivalent electrons, and ii) the system is made up of equivalent electrons.

We begin with looking at a configuration of two non-equivalent p -electrons, *i.e.* the configuration $npn'p$. The possible values of L , S , M_L and M_S are:

$$\left. \begin{array}{l} L = |1-1|, \dots, 1+1 = 0, 1, 2 \\ S = |1/2-1/2|, \dots, 1/2+1/2 = 0, 1 \\ M_L = -2, \dots, 2 \\ M_S = -1, 0, 1 \end{array} \right\} \quad (7.6)$$

We now construct a $M_L M_S$ table to be able to identify the different terms.

Table MLMS

Starting in the upper left corner it is seen that the only term that can be in this state is 3D ($1 \uparrow 1 \uparrow$). This term (3D) will contribute with one state to each box in the table. The next box to the right has two states, one from 3D and one from the only other available namely 1D . 1D will contribute with one state to all singlet ($\uparrow\downarrow$), ($\downarrow\uparrow$) boxes. The $M_L = 2$, $M_S = -1$ box already has its state from 3D . The $M_L M_S = 11$ box need one more state which only can come from 3P (and this term will contribute with one state to the 11, 1-1, 01, 00, -11, -10 and -1-1 boxes). Continuing

this reasoning we see that all 36 $((3^*2)(3^*2))$ states can be accounted for with the 3D , 1D , 3P , 1P , 3S and 1S terms. Thus, we see that the $1/r_{12}$ operator (electrostatic interaction) will split the $npn'p$ configuration into six different eigenstates.

Next we look at two equivalent p -electrons. The Pauli-exclusion principle will now reduce the number of states in the table because for example $(1 \uparrow 1 \uparrow)$ and $(0 \downarrow 0 \downarrow)$ are both forbidden. We also realize that the order in which the states appear in the table does not matter when we deal with equivalent electrons so for example $(1 \uparrow -1 \uparrow)$ is the same as $(-1 \uparrow 1 \uparrow)$, and one of the has to be removed. The same reasoning as in the non-equivalent electron case now obviously lead to the terms 1D , 3P and 1S . We conclude that the electrostatic interaction will split a system of two equivalent p -electrons into three levels (eigenstates).

7.2 The spin-orbit interaction

The spin-orbit operator is essentially $l_i \cdot s_i$ and in the JM -representation a typical matrix element take the form

$$\begin{aligned} \langle \gamma' L' S' J' M' | l_i \cdot s_i | \gamma L S J M \rangle &= \delta_{M' M} \delta_{J' J} (-1)^{L+S'+J} \begin{Bmatrix} L' & L & 1 \\ S & S' & J \end{Bmatrix} \times \\ \sum_{\gamma''} \langle \gamma' L' || l_i || \gamma'' L \rangle \langle \gamma'' S' || s_i || \gamma S \rangle \end{aligned} \quad (7.7)$$

where we have used Eq. (6.25) with $k = 1$. The delta function and the $6j$ -symbol in Eq. (7.7) give us the following selection rules for the spin-orbit matrix element,

$$\left. \begin{aligned} \Delta M &= 0 \\ \Delta J &= 0 \\ \Delta S &= 0, \pm 1 \\ \Delta L &= 0, \pm 1 \end{aligned} \right\} \quad (7.8)$$

As for the electrostatic interaction, the matrix elements of the spin-orbit operator is independent of the quantum number M , *i.e.* the situation is spherically symmetric. The effect of this operator is to split up the terms into multiplets (fine structure) characterized by J . The term symbol can be used to describe these multiplets provided we add the J quantum number

$$^{2S+1}L_J \quad (7.9)$$

Because $J = |L - S|, \dots, L + S$ the $2L + 1$ (or $2S + 1$ depending on if $L > S$ or not) degeneracy is lifted by the spin-orbit interaction.

7.3 The crystal-field interaction

So far both interaction studied have been spherically symmetric and therefore the corresponding matrix elements have not been dependent on the quantum numbers

M_L , M_S or M_J . In this section the effects of the crystal field will be discussed, and by this we mean the effect of the other ions in the system. Our Hamiltonian is no longer spherically symmetric (*c.f.* a site with for example cubic symmetry) and we should therefore expect M dependent matrix elements.

The crystal field Hamiltonian can be written

$$H_{cf} = -e \sum_{ikq} A_{kq} r_i^k Y_{kq}(\theta_i \varphi_i) \quad (7.10)$$

where i run over all ions in the system and A_{kq} are the so called crystal field parameters. It should be noted that Eq. (7.10) represent only the most simple and naive parameterizations of the crystal field. There exist more sophisticated models, *e.g.* correlated crystal field models. The book by Ng and Newman [10] (2000) “Crystal field handbook” is recommended for the curious reader.

From Eq. (7.10) we see that the radial and the angular parts can be treated separately. The radial part becomes

$$\langle n'l' | r_i^k | nl \rangle \quad (7.11)$$

and for the angular part we obtain, in $M_L M_S$ -representation,

$$A_{kq} \langle \gamma' S' L' M'_S M'_L | Y_{kq} | \gamma S L M_L M_S \rangle = \delta_{S'S} \delta_{M'_S M_S} (-1)^{L'-M'_L} \times \\ \begin{pmatrix} L' & k & L \\ -M'_L & q & M_L \end{pmatrix} \langle \gamma' L' || Y_k || \gamma L \rangle A_{kq} \quad (7.12)$$

Once again the power of the Wigner-Eckart theorem can be appreciated. All the M dependencies has been contained in the $3j$ -symbol! The $3j$ -symbol put the following constraints on Eq. (7.12) for the expression to be non-zero in the case of equivalent electrons

$$\left. \begin{array}{l} -M'_L + q + M_L = 0 \\ 0 \leq k \leq 2L \\ k \text{ even} \end{array} \right\} \quad (7.13)$$

The reduced matrix elements in Eq. (7.12) is straight forward to evaluate using Eq. (6.28) when we work with two equivalent electrons. We will later on in the course, if time permits, look at the techniques needed when we have more then two equivalent electrons. Applying Eq. (7.12) essentially reduce the problem to evaluating the Gaunt's coefficients, Eq. (6.10).

So far we have not used the symmetry of the crystal field to reduce the labour needed in our calculations. At a first glance at Eqs. (7.12) and (7.10) the number of terms (combinations of kq) seem very large. k is constrained by Eq. (7.13) but the number of terms is still large. By realizing that also q can be constrained due to symmetry considerations, we save a lot of computation. The φ -dependence for $Y_{kq}(\theta\varphi)$ is $\exp(iq\varphi)$ so for example a crystal field that has trigonal symmetry around the z -axis must satisfy

$$V(r\theta\varphi + \frac{2\pi}{3}) = V(r\theta\varphi)$$

which means that q in this case only takes the values $q = 0, \pm 3, \pm 6, \dots$. Sixfold symmetry would give $q = 0, \pm 6, \dots$ and fourfold symmetry would give $q = 0, \pm 4, \pm 8, \dots$. If we want to investigate an f -electron system in a hexagonal field we do therefore only have to consider the terms

$$V = A_{20}r^2Y_{20} + A_{40}r^4Y_{40} + (A_{6-6}Y_{6-6} + A_{60}Y_{60} + A_{66}Y_{66})r^6$$

The $A_{00}Y_{00}$ contribution is spherical and does therefore not contribute to the splitting, it only move the configuration as a whole.

We conclude by emphasizing that the effect of the crystal field Hamiltonian (H_{CF}) is to split up the term into energy levels characterized by M_L

7.4 The Zeeman effect

From some course in classical physics one might remember that the energy for a dipole in an external magnetic field (B) is given by

$$W_m = -\mu \cdot B \quad (7.14)$$

Choosing $B = B\hat{z}$ and assuming Eq. (7.14) valid also in quantum mechanics, one get with

$$\mu = \mu_B(-L - 2S) \quad (7.15)$$

and

$$H_m = \mu_B B(L_z + 2S_z) \quad (7.16)$$

A general matrix element of H_m between two multiplets now becomes trivial to calculate using the machinery developed so far.

$$\begin{aligned} \langle \gamma' S' L' J' M' | H_m | \gamma S L J M \rangle &= \mu_B B \langle \gamma' S' L' J' M' | L_z | \gamma S L J M \rangle \\ &+ 2\mu_B B \langle \gamma' S' L' J' M' | S_z | \gamma S L J M \rangle \end{aligned} \quad (7.17)$$

By applying the Wigner-Eckart theorem and Eqs. (6.28) and (6.29) we get for the matrix elements on the right hand side of Eq. (7.17)

$$\langle \gamma' S' L' J' M' | L_z | \gamma S L J M \rangle = (-1)^{J'-M'} \begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix} \langle \gamma' S' L' J' || L || \gamma S L J \rangle \quad (7.18)$$

and the reduced matrix element can be simplified to

$$\langle \gamma' S' L' J' || L || \gamma S L J \rangle = (-1)^{L'+S+J+1} \sqrt{[J'] [J]} \left\{ \begin{matrix} L' & L & 1 \\ J & J' & S \end{matrix} \right\} \langle \gamma' L' || L || \gamma L \rangle \delta_{S'S} \quad (7.19)$$

The spin part of the problem is equally straight forward

$$\langle \gamma' S' L' J' M' | S_z | \gamma S L J M \rangle = (-1)^{J'-M'} \begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix} \langle \gamma' S' L' J' || S || \gamma S L J \rangle \quad (7.20)$$

and the reduced matrix element of S can be simplified to

$$\langle \gamma' S' L' J' || S || \gamma S L J \rangle = (-1)^{L+S+J'+1} \sqrt{[J'] [J]} \left\{ \begin{matrix} S' & S & 1 \\ J & J' & L \end{matrix} \right\} \langle \gamma' S' || S || \gamma S \rangle \delta_{L'L} \quad (7.21)$$

The reduced matrix elements on the right hand side of Eqs. (7.19) and (7.21) are obtained by noting that

$$\langle \gamma' J' M' | J_z | \gamma J M \rangle = (-1)^{J'-M'} \begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix} \langle \gamma' J' || J || \gamma J \rangle \quad (7.22)$$

where

$$\langle \gamma' J' || J || \gamma J \rangle = \frac{\langle \gamma' J' M' | J_z | \gamma J M \rangle}{(-1)^{J'-M'} \begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix}} = \frac{m\hbar \overbrace{\langle \gamma' J' M' | \gamma J M \rangle}^{\delta_{\gamma'\gamma} \delta_{J'J} \delta_{M'M}}}{(-1)^{J'-M'} \begin{pmatrix} J' & 1 & J \\ -M' & 0 & M \end{pmatrix}} \quad (7.23)$$

For $M' = J'$ and $J = M$ in Eq. (7.22) we get using the Wigner-Eckart theorem

$$\langle \gamma' J' J' | J_z | \gamma J J \rangle = (-1)^{J'-J} \begin{pmatrix} J' & 1 & J \\ -J' & 0 & J \end{pmatrix} \langle \gamma' J' || J || \gamma J \rangle \quad (7.24)$$

and the corresponding reduced matrix element is given by

$$\langle \gamma' J' || J || \gamma J \rangle = \frac{J\hbar \delta_{\gamma'\gamma} \delta_{J'J} \delta_{M'M}}{(-1)^{J'-J} \begin{pmatrix} J' & 1 & J \\ -J' & 0 & J \end{pmatrix}} \quad (7.25)$$

Eqs. (7.23) and (7.25) give

$$\begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} = \frac{M}{J} (-1)^{-J+M} \begin{pmatrix} J & 1 & J \\ -J & 0 & J \end{pmatrix} \quad (7.26)$$

It can also be shown that

$$\begin{pmatrix} J & 1 & J \\ -J & 0 & J \end{pmatrix} = \sqrt{\frac{J}{(J+1)(2J+1)}} \quad (7.27)$$

and Eq. (7.23) therefore finally become

$$\langle \gamma' J' || J || \gamma J \rangle = \sqrt{J(J+1)(2J+1)} \delta_{\gamma'\gamma} \delta_{J'J} \quad (7.28)$$

Eqs. (7.17), (7.18)-(7.21) and (7.28) put together give us the general expression for $\langle \gamma' S' L' J' M' | H_m | \gamma S L J M \rangle$ and the Zeeman problem is solved!

Bibliography

- [1] H. W. Wyld, *Mathematical methods for physics* (Addison-Wesley Publishing Company, Inc., New York, 1976).
- [2] G. Arfken, *Mathematical methods for physicists* (Academic Press, Inc., New York, 1985).
- [3] G. Racah, Phys. Rev. **62**, 438 (1942).
- [4] E. U. Condon and G. H. Shortley, *The theory of atomic spectra* (Cambridge university press, London, 1935).
- [5] Wigner.
- [6] G. Racah, Phys. Rev. **61**, 186 (1942).
- [7] G. Racah, Phys. Rev. **63**, 367 (1943).
- [8] G. Racah, Phys. Rev. **76**, 1352 (1949).
- [9] B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).
- [10] D. J. Newman and B. Ng, *Crystal Field Handbook*.
- [11] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1974).